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BY

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THE EXPLOSION AND FIRE HAZARDS OF HYDROCARBON-CARBON TETRACHLORIDE MIXTURES[1]

By G. W. Jones[2] and R. E. Kennedy[3]

INTRODUCTION

Most gasolines and naphthas are mixtures of paraffin-series hydrocarbons nd comprise such substances as pentane, hexane, heptane, octane, and others p to perhaps dodecane. Many of these hydrocarbons, when mixed with the roper proportions of air and ignited, are highly explosive. It is due to his characteristic that gasoline has become so important as a fuel in nternal-combustion engines. Gasoline and naphtha also are used in the industry as solvents and cleaning agents. Because of their explosive properties hey are dangerous to use unless the composition is so chosen that the vapor ressure of the mixture is not high enough to produce explosive mixtures with ir at the temperature at which they are used.

Hydrocarbon mixtures may be made less hazardous by adding some incombusible liquid, such as carbon tetrachloride. Barrier[4] reports the amount of arbon tetrachloride that must be added to different naphthas to render such ixtures free from fire and explosion hazards. He found that the amount of arbon tetrachloride that must be present in the final mixture of naphtha and arbon tetrachloride varied with the density of the naphtha. Of the naphthas ested the amount of carbon tetrachloride necessary to render such mixtures ree from fire and explosion hazards ranged from 30 to 70 percent.

Determination of the fire and explosion hazards of carbon tetrachloride-ydrocarbon mixtures would be easy if the boiling points and vapor pressures f the two were the same at any given temperature. The fact that carbon etrachloride boils at 76° C. while the boiling points of the hydrocarbons ound in gasoline and naphtha may range from 37°, the boiling point of pentane,

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Barrier, E. A., Flash, Fire, and Explosion Tests on Mixtures of Carbon Tetrachloride and Naphtha: Ind. Eng. Chem., vol. 2, 1910, p. 16.

to above 200° C. (dodecane boils at 214.5° C.) complicates determination of the fire and explosion hazards of such mixtures. If a mixture of pentane (boiling point, 37° C.) and carbon tetrachloride (boiling point, 76° C.) is placed in an open container the constituent having the higher vapor pressure evaporates more rapidly than that with a lower vapor pressure, so that the vapor arising from the liquid mixture is not the same in composition as the liquid mixture remaining. Therefore, tests at different periods of time after the liquid has been exposed to the atmosphere will give different results.

Tests were made to determine the ability of carbon tetrachloride-hydrocarbon mixtures to form flammable mixtures when completely vaporized and mixed with air. Glass explosion tubes 40 to 50 cm long and 3.5 to 4.0 cm inside diameter were prepared. One end was sealed off while the other was closed with a tight-fitting cork. Six or eight glass beads were placed in the tube to facilitate mixing the gases and vapors. Mixtures of the several hydrocarbons--pentane, hexane, heptane, octane, naphtha, and gasoline--with various amounts of carbon tetrachloride were prepared and tested in these tubes for flammability. Since preliminary tests showed that 50 percent or more of carbon tetrachloride by volume must be present in the final liquid mixtures to prevent explosions when mixed with air only such mixtures were tested.

The explosion tubes ranged in capacity from 475 to 540 cm³. Two or three drops of the pure hydrocarbons gave flammable mixtures when vaporized in the tube. In testing any particular hydrocarbon-carbon tetrachloride mixture, the explosion tube was placed vertically with the open end at the top. The tube was purged of combustion products from a previous test by sweeping out with compressed air for 1 minute. Then 2 drops of the particular test mixture were dropped into the tube from a 1-cm³ pipette, the tube was closed with the cork stopper and the liquid vaporized by shaking with the glass beads in the tube. Complete vaporization and mixing required 1 to 2 minutes. The tube was then mounted in vertically with the stoppered end at the bottom.

A test for flammability was made in a darkened room by removing carefully the stopper and passing the flame from an alcohol lamp across the open end of the tube. If the mixture were flammable, flame would pass from the open end through the tube. If 2 drops failed to produce a flammable mixture the amount of liquid added was increased and the test repeated.

In testing the flammability of hexane the following tests were made in a tube of 475 cm³ capacity:

No. of drops added to explosion tube	Did flame propagate through mixture
1	No.
2	No.
4	Yes.
8	Yes.
10	Yes.
11	Yes.
12	No - burned at open end only.

Tests with a mixture containing 50 percent hexane and 50 percent carbon tetrachloride gave the following results:

No. of drops added to explosion tube	Did flame propagate through mixture?
2	No.
4	No.
6	No.
8	Green flame 2/3 way up tube.
9	Yes.
12	Yes.
16	Yes.
20	Yes.
24	Yes.
25	No.

These tests showed that the 50-50 mixture of hexane and carbon tetrachloride produced flammable mixtures with air within the limits given above. Similar tests were made with mixtures in which the proportions of carbon tetrachloride were increased until the resulting mixture was not flammable regardless of the number of drops of liquid added to the explosion tube.

A summary of such tests with pentane, hexane, heptane, octane, one sample of solvent naphtha, and motor gasoline is given in table 1. Since the flammable properties of naphthas and gasolines are due largely to the presence of hydrocarbons ranging from pentane to octane tests were confined largely to these pure hydrocarbons.

Table 1 shows that, with the exception of the gasoline, there must be 66.7 to 70 percent carbon tetrachloride by volume present in the mixture to prevent propagation of flame. For the gasoline tested there must be at least 58 percent of carbon tetrachloride in the final mixture to prevent propagation of flame. Less carbon tetrachloride is required for gasoline than for the pure hydrocarbons tested because about 30 percent of the gasoline had a boiling point above 150° C., and consisted of hydrocarbons having a molecular weight higher than octane. These hydrocarbons have low vapor pressures, and it was impossible to vaporize them completely in the explosion tube.

The results given in table 1 (with the exception of gasoline) represent conditions in which the mixtures were vaporized completely so that the proportions in the original mixtures were the same as in the vapor arising from the mixture.

TABLE 1. - Flammability of hydrocarbon-carbon tetrachloride mixtures

Hydrocarbon	Formula	Percent by volume						
		50.0 CCl_4 50.0 H.C.*	58.0 CCl_4 42.0 H.C.	62.5 CCl_4 37.5 H.C.	63.5 CCl_4 36.5 H.C.	66.7 CCl_4 33.3 H.C.	70.0 CCl_4 30.0 H.C.	75.0 CCl_4 25.0 H.C.
Pentane[1]	C_5H_{12}	Yes.	Yes.	Yes.	Yes.	No.	No.	No.
Hexane[2]	C_6H_{14}	Yes.	Yes.	Yes.	Yes.	Yes.	No.	No.
Heptane[3]	C_7H_{16}	Yes.	Yes.	Yes.	Yes.	Yes.	No.	No.
Octane[4]	C_8H_{18}	Yes.	Yes.	Yes.	Yes.	No.	No.	No.
Naphtha[5]	-	Yes.	Yes.	Yes.	Yes.	Yes.	No.	No.
Gasoline[6]	-	Yes.	No.	No.	No.	No.	No.	No.

* H.C. = Hydrocarbons.

[1] Pentane - "Practical" Eastman Kodak Co. boiling point, 33° to 36° C.

[2] Hexane - "Practical" Eastman Kodak Co. boiling point, 65° to 70° C.

[3] Heptane - "Practical" Eastman Kodak Co. boiling point, 91° to 96° C.

[4] Octane - From petroleum boiling point, 100° to 125° C.

[5] Naphtha - Solvent - Initial boiling point, 97° C.

10 percent	101
50 percent	112
95 percent	153
End point	155

[6] Gasoline - Initial boiling point, 31° C.

10 percent	57
50 percent	124
70 percent	149
90 percent	183
End point	205
Specific gravity	0.729

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To obtain information concerning the fire hazard or combustibility of the different hydrocarbons when mixed with carbon tetrachloride under conditions where the liquid is placed in open storage the following tests were made:

One cm^3 of each test mixture given in table 1 was poured into a watch glass and ignited with the flame from a burning match. Notations were made as to whether the mixture continued to burn after the ignition source was removed and, if so, how long. The results of these tests are given in table 2.

Pentane, which has a boiling point considerably below that of carbon tetrachloride, burned with a steady flame, even when the mixture contained 75 percent carbon tetrachloride by volume, due to the fact that the vapors arising from the liquid contained a smaller proportion of carbon tetrachloride vapor than the original mixture.

For hexane, the mixtures would not burn with a steady flame when the proportions of carbon tetrachloride exceeded about 62.5 percent. Above this percentage the mixtures would burn only when the igniting flame was held just above the surface of the liquid. For the other hydrocarbons, the mixtures need contain only 50 percent carbon tetrachloride to prevent steady burning of the liquids.

Some hydrocarbons having a low vapor pressure, such as dodecane, will not produce flammable mixtures when shaken with air and will not burn at the usual laboratory temperatures when the liquid is placed in an open container and an ignition source brought in contact with the surface. However, if these hydrocarbons are spread out on material whereby they are subdivided into thin layers or particles (as, for example, on a wick), the hydrocarbons will burn readily when ignited. To investigate the burning hazards that might arise when hydrocarbons are spilled on floors or on waste material the following tests were made: The various mixtures given in table 1 were tested for their ability to burn by dipping one end of a 1/4-inch round asbestos wick 2.5 cm into the liquid mixtures and then lighting the wick with the flame from a burning match. Notations were made as to whether the mixture burned steadily on the wick. If the mixtures burned 5 seconds or longer after ignition the results were recorded as "steady burning" and are so noted in table 3. If the mixtures only burned from 1 to 2 seconds after ignition the results have been recorded as "momentary flame", and if they burned for less than 1 second as "no flame".

In general, these tests showed that a higher percentage of carbon tetrachloride is required in the mixture to prevent burning on a wick than is required to prevent burning in an open dish.

TABLE 2. – Burning tests in open dish

Hydrocarbon	Formula	Boiling point, °C.	Percent by volume 50.0 CCl_4 50.0 H.C.*	 53.0 CCl_4 42.0 H.C.	 62.5 CCl_4 37.5 H.C.	 63.5 CCl_4 36.5 H.C.	 66.7 CCl_4 33.3 H.C.	 70.0 CCl_4 30.0 H.C.	 75.0 CCl_4 25.0 H.C.
Pentane	C_5H_{12}	37	Steady flame.	Steady flame.	Steady flame.	Steady flame.	Steady flame.	Steady flame.	Steady flame.
Hexane	C_6H_{14}	69	do.	do.	do.	Burned for about 1 second.	Momentary flame.	Momentary flame.	No flame.
Heptane	C_7H_{16}	98	Momentary flame.	Momentary flame.	No flame.	No flame.	No flame.	No flame.	do.
Octane	C_8H_{18}	125	No flame.	No flame.	do.	do.	do.	do.	do.
Naphtha	–	–	do.	do.	do.	do.	do.	do.	do.
Gasoline	–	–	Momentary flame.	Momentary flame.	Momentary flame.	Momentary flame.	do.	do.	do.

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* H.C. = Hydrocarbons.

TABLE 3. - Burning tests using 1/4-inch round asbestos wick

		Percent by volume						
Hydrocarbon	Formula	50.0 CCl_4 50.0 H.C.*	58.0 CCl_4 42.0 H.C.	62.5 CCl_4 37.5 H.C.	63.5 CCl_4 36.5 H.C.	66.7 CCl_4 33.3 H.C.	70.0 CCl_4 30.0 H.C.	75.0 CCl_4 25.0 H.C.
Pentane	C_5H_{12}	Steady flame.	Steady flame.	Steady flame.	Steady flame.	Steady flame.	Burned 4 seconds.	Burned 2 seconds after match removed.
Hexane	C_6H_{14}	do.	do.	do.	do.	Burned 2 seconds.	Burned 1 second.	Momentary flame.
Heptane	C_7H_{16}	do.	Momentary flame.	Momentary flame.	No flame.	No flame.	No flame.	No flame.
Octane	C_8H_{18}	do.	Steady flame.	Steady flame.	Steady flame.	Burned 2 seconds.	do.	do.
Naphtha	-	do.	Momentary flame.	No flame.	No flame.	No flame.	do.	do.
Gasoline	-	do.	No flame.	do.	do.	do.	do.	do.

* H.C. = Hydrocarbons.

A general summary of the results obtained by the different tests is in table 4.

TABLE 4. - Results showing amounts of carbon tetrachloride that must be present in final mixture by volume to render such mixtures nonflammable and incapable of supporting combustion, percent

Hydrocarbon	Explosion-tube tests Amount of CCl_4 that must be present to prevent flammability with air	Open-dish tests Amount of CCl_4 that must be present to prevent burning in open containers	Wick tests Amount of CCl_4 t must be present prevent burnin on wicks
Pentane	66.7	80.0	70.0
Hexane	70.0	63.5	66.7
Heptane	70.0	50.0	58.0
Octane	66.7	50.0	66.7
Naphtha	70.0	50.0	58.0
Gasoline	58.0	50.0	58.0

CONCLUSIONS

This investigation shows that to eliminate the fire and explosion haza of hydrocarbons ranging from hexane to octane the final mixtures must contai at least 70 percent by volume of carbon tetrachloride.

Gasoline and naphtha, since different brands may vary in composition, should contain 70 percent of carbon tetrachloride by volume in the final mi ture.

Pentane-carbon tetrachloride mixtures must contain at least 80 percent carbon tetrachloride to prevent burning in an open vessel.

Owing to the fact that the rate of evaporation of carbon tetrachloride and the hydrocarbons may not be the same at a given temperature, the residu hydrocarbon-carbon tetrachloride mixtures, if left in open containers, will change in composition over periods of time. Hydrocarbons having a boiling point above that of carbon tetrachloride will have higher percentages of hy carbons in the residual mixture after being exposed in the open air and eventually may become flammable and capable of supporting combustion. For this reason it will be necessary to add carbon tetrachloride from time to t to maintain its concentration sufficiently high to prevent flammability and burning.